d^0 Alkane Complexes ($^tBu_3SiN{=})_3W(RH)$ Precede C−H Activation and Formation of ($^tBu_3SiN{=})_2(^tBuSiNH)WR/R'$

Daniel F. Schafer II and Peter T. Wolczanski*

Baker Laboratory, Department of Chemistry
Cornell University, Ithaca, New York 14853

Received January 12, 1998

The existence of alkane complexes and their plausible connection to alkane activation products has commanded considerable attention. A limited number of alkane complexes have been observed at low temperatures in hydrocarbon and liquified noble gas matrixes,[1,2] while the detection of {η^2-HB(3,5-dimethylpyrazolyl)$_3$}Rh(CO)(CyH)) by ultrafast spectroscopy, and its conversion to {η^3-HB(3,5-dimethylpyrazolyl)$_3$}Rh(CO)(H)Cy, constitutes a direct observation under reaction conditions.[3] Equilibria implicate the presence of *trans*-($^iPr_3P)_2X(H)_2Ir(RH)$,[4] but evidence of $L_nM(RH)$ is often predicated on isotopomer interconversions of suitably labeled $L_nM(H)R$.[5−14] These inferences have been applied principally to d^n ($n \geq 4$) systems (e.g., Cp*Ir(PR_3)[5] and Cp*$_2$W),[9] yet for alkane 1,2-additions[15−18] to transient d^0 imido species (e.g., ($^tBu_3SiO)_2Ti{=}NSi^tBu_3$),[15] computational predictions of $L_nM(RH)$[19] have no experimental support. Herein the generation of various ($^tBu_3SiN{=})_2(^tBu_3SiNH)WR$ (**1**−R) species are rationalized via the intermediacy of ($^tBu_3SiN{=})_3W(RH)$ (**2**−RH).

Treatment of $NaW_2Cl_7(THF)_5$[20] with 6 equiv of $^tBu_3SiNHLi$ in benzene afforded ($^tBu_3SiN{=})_2(^tBu_3SiNH)WH$ (**1**−H) in 60% yield according to eq 1.[21] Deprotonation with excess KH in THF produced solvent-free [($^tBu_3SiN{=})_3WH]K$ (**2**−KH, 80%) upon isolation from Et_2O (eq 2).[22] **1**−H and **2**−KH exhibit diagnostic

$$NaW_2Cl_7(THF)_5 + 6\,^tBu_3SiNHLi \xrightarrow[\text{(2) 100 °C, 6 h}]{\text{(1) } C_6H_6\text{, 23 °C, 1 h}} \underset{\mathbf{1}-H}{2(^tBu_3SiN{=})_2(^tBu_3SiNH)WH} \quad (1)$$

$$\mathbf{1}-H + KH \xrightarrow[-H_2]{\text{THF, 23 °C, 48 h}} \underset{\mathbf{2}-KH}{[(^tBu_3SiN{=})_3WH]K} \quad (2)$$

^{1}H NMR resonances at δ 13.34 (J_{WH} = 356 Hz) and 7.11 (J_{WH} = 313 Hz), and corresponding infrared ν(WH) of 1930 and 1858 cm^{-1}, respectively. Both hydrides are hydrocarbon soluble, implicating binding of K^+ to the [($^tBu_3SiN{=})_3WH]^-$ core of **2**−KH. **1**−H was converted to ($^tBu_3SiN{=})_2(^tBu_3SiNH)WX$ (**1**−X, X = Cl, I) via addition of CX_4, and exposure of **1**−X to appropriate alkyllithium reagents led to ($^tBu_3SiN{=})_2(^tBu_3SiNH)$-WR (**1**−R, R = CH_3, CD_3, aryl, etc.). Thermolysis of **1**−R for prolonged periods at >200 °C failed to induce 1,2-RH-elimination, consistent with the increased barrier to alkane/arene loss upon proceeding from group 4 to group 6.[15,23]

The reactivity of primary alkyl halides with [($^tBu_3SiN{=})_3WH]K$ (**2**−KH) provided evidence of alkane complexation, as the general mechanism in Scheme 1 and product distributions in Table 1 indicate. Entries 1 and 2 show that exposure of **2**−KH to CH_3I resulted in ($^tBu_3SiN{=})_2(^tBu_3SiNH)WCH_3$ (**1**−CH_3, 90%),[24] but use of CD_3I produced two isotopomers, **1**−CD_3 and ($^tBu_3SiN{=})_2$-($^tBu_3SiND)WCHD_2$ (**1**−ND−CHD_2), consistent with the intermediacy of ($^tBu_3SiN{=})_3W(CHD_3)$ (**2**−CHD_3). The k_H/k_D determined from ^{2}H NMR analysis of the **1**−ND−CHD_2:**1**−CD_3 ratio was 9.6(6), a plausible value for partitioning from **2**−CHD_3.[25] A small amount of solvent-activated product, ($^tBu_3SiN{=})_2(^tBu_3$-$SiND)WC_6D_5$ (**1**−ND−Ph-d_5, ∼10, 27%),[26] is produced, presumably due to competing methane loss from **2**−CH_4 or **2**−CHD_3. In a parallel reaction of **2**−KH, CD_3I, and 4 equiv of CH_4 (entry 3), no incorporation of CH_4 was detected (<10%), ruling out competitive activation of free CD_3H and CH_4 in C_6D_6. No amide/methyl scrambling was evident upon prolonged (6 d, 200 °C) thermolysis of independently prepared **1**−CD_3, and no C−H bond activation chemistry was observed in thermolyses of **2**−KH and [($^tBu_3SiN{=})_3WI]K$ (**2**−KI) in C_6D_6.[27]

(1) (a) Perutz, R. N.; Belt, S. T.; McCamley, A.; Whittlesey, M. K. *Pure Appl. Chem.* **1990**, *62*, 1539−1545. (b) Perutz, R. N. *Chem. Soc. Rev.* **1993**, *22*, 361−369.

(2) (a) Schultz, R. H.; Bengali, A. A.; Tauber, M. J.; Weiller, B. H.; Wasserman, E. P.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7369−7377. (b) Bengali, A. A.; Schultz, R. H.; Bergman, R. G.; Moore, C. B. *J. Am. Chem. Soc.* **1994**, *116*, 9585−9589.

(3) Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B. D.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260−263 and references therein.

(4) (a) Lee, D. W.; Jensen, C. M. *J. Am. Chem. Soc.* **1996**, *118*, 8749−8750. (b) Lee, D. W.; Jensen, C. M. *Inorg. Chim. Acta* **1997**, *259*, 359−362.

(5) Mobley, T. A.; Schade, Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 7822−7823.

(6) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332−7346.

(7) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537−1550.

(8) Bloyce, P. E.; Rest, A. J.; Whitwell, I. *J. Chem. Soc., Dalton Trans.* **1990**, 813−822.

(9) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172−1179.

(10) Gould, G. L.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 5502−5504.

(11) Bullock, R. M.; Headford, C. E. L.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 727−729.

(12) Chernega, A.; Cook, J.; Green, M. L. H.; Labella, L.; Simpson, S. J.; Souter, J.; Stephens, A. H. H. *J. Chem. Soc., Dalton Trans.* **1997**, 3225−3243.

(13) (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961−5976. (b) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848−849.

(14) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* **1997**, *265*, 117−125.

(15) Bennett, J. L.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1997**, *119*, 10696−10719.

(16) Schaller, C. P.; Cummins, C. C.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1996**, *118*, 591−611.

(17) de With, J.; Horton, A. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 903−905.

(18) Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1993**, *32*, 131−144.

(19) Cundari, T. R. *Organometallics* **1993**, *12*, 1998−2000.

(20) Chisholm, M. H.; Eichorn, B. W.; Folting, K.; Huffman, J. C.; Ontiveros, C. D.; Streib, W. E.; Van Der Sluys, W. G. *Inorg. Chem.* **1987**, *26*, 3182−3186.

(21) **1**−H: ^{1}H NMR (C_6D_6, 23 °C) δ 1.18 (s, ^{t}Bu, 27 H), 1.34 (s, ^{t}Bu, 54 H), 7.41 (s, NH, 1 H), 13.34 (WH, J_{WH} = 356 Hz); ^{13}C{^{1}H} NMR δ 22.72 (HNSiC), 23.95 (=NSiC), 30.53 (HNSiCCH_3), 31.11 (=NSiCCH_3). Anal. Calcd for $H_{83}C_{36}N_3Si_3W$: C, 52.34; H, 10.13; N, 5.09. Found: C, 51.71; H, 10.53; N, 5.01.

(22) **2**−KH: ^{1}H NMR (C_6D_6, 23 °C) δ 1.40 (s, ^{t}Bu, 81 H), 7.11 (WH, J_{WH} = 313 Hz); ^{13}C{^{1}H} NMR δ 23.95 (SiC), 31.63 (CH_3). Anal. Calcd for $H_{82}C_{36}N_3Si_3KW$: C, 50.03; H, 9.56; N, 4.86. Found: C, 50.19; H, 10.03; N, 4.69.

(23) Morrison, D. L.; Rodgers, P. M.; Chao, Y.-W.; Bruck, M. A.; Grittini, C.; Tajima, T. L.; Alexander, S. J.; Rheingold, A. L.; Wigley, D. E. *Organometallics* **1995**, *14*, 2435−2446.

(24) **1**-Me: ^{1}H NMR (C_6D_6, 23 °C) δ 1.19 (s, ^{t}Bu, 27 H), 1.33 (s, ^{t}Bu, 54 H), 1.43 (WMe, J_{WH} = 11 Hz), 6.59 (s, NH, 1 H); ^{13}C{^{1}H} NMR δ 21.62 (WCH_3, J_{WC} = 138 Hz), 23.38 (HNSiC), 24.55 (=NSiC), 30.72 (HNSiCCH_3), 31.26 (=NSiCCH_3).

(25) (a) Schaller, C. P.; Bonanno, J. B.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1994**, *116*, 4133−4134. (b) Preliminary measurements on (silox)$_2$-($^tBu_3SiH)TiCH_nD_{3-n}$ (n = 0−2) ⇌ (silox)$_2$($^tBu_3SiD)TiCH_nD_{3-n}$ (n = 1−3) indicate the EIEs are ∼1, neglecting statistical factors. Slaughter, L. M.; Wolczanski, P. T. Unpublished results.

(26) **1**−Ph: ^{1}H NMR (C_6D_6, 23 °C) δ 1.19 (s, ^{t}Bu, 27 H), 1.36 (s, ^{t}Bu, 54 H), 6.90 (s, NH, 1 H), 7.02 (t, *p*-CH, 1 H, J = 7 Hz), 7.22 (m, *m*-CH, 2 H), 8.45 (d, *o*-CH, 2 H, J = 7 Hz); ^{13}C{^{1}H} NMR δ 23.56 (=NSiC), 24.57 (HNSiC), 30.79 (=NSiCCH_3), 31.30 (HNSiCCH_3), 129.16, 143.44 (C_{ortho}, C_{meta}), 174.50 (C_{ipso}, J_{WC} = 181 Hz).

S0002-7863(98)00115-2 CCC: $15.00
Published on Web 05/05/1998

Scheme 1

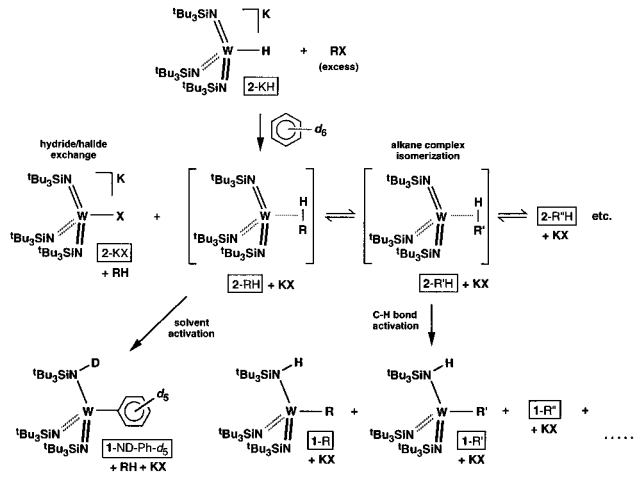
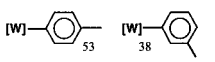
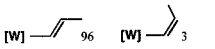
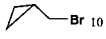
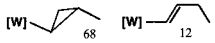
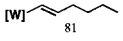


Table 1. Product Distribution[a] from the Reaction of [(^{t}Bu$_3$SiN=)$_3$WH]K (**2**−KH) with RX According to Scheme 1

entry	RX (equiv)	time (h), T (°C)	product distribution, %[b] 2-KX	1-ND-Ph-d_5	1-R	1-R′/R″
1)	CH_3I (10)	8, 60	<2	10	90	-
2)	CD_3I (10)	8, 60	<2	27	56[c]	**1**-ND-CHD_2, 17[c]
3)	CD_3I (10)	8, 60	<9	26		65, total **1**-CD_3 + **1**-ND-CHD_2[d]
	CH_4 (4, 3 atm)					
4)	CH_3CH_2I (10)	10, 100	27[e]	23	30	
5)	CD_3CH_2I (10)	10, 100	37[e]	26	14	**1**-ND-CD_2CH_3, 2
6)	 10	13, 25[f]	9	<2	-	 53 38
7)	 5	8, 60[g]	<2	<2	-	 96 3
8)	 10	6, 100	20	<2	-	 68 12
9)	 10	24, 100	9[e]	<2	-	 81

[a] Analysis by ^{1}H NMR unless otherwise noted. [b] [W] = (^{t}Bu$_3$SiN=)$_2$(^{t}Bu$_3$SiNH)W. [c] **1**−CD_3:**1**−ND−CHD_2 determined by ^{2}H NMR. [d] Analysis of the NH resonance of **1**−CD_3 by ^{1}H NMR indicated the same amount as in entry 3, and no W-CH_3 singlet was observed. [e] (^{t}Bu$_3$SiN=)$_2$(^{t}Bu$_3$SiNH)WX (**1**−X) was present (entry 4, 21%; entry 5, 21%; entry 9, 11%). [f] When performed in toluene-d_8, no solvent incorporation was noted; the same product ratio was observed. [g] **1**−*cis*-CH=CHMe may be photochemically derived from **1**−*trans*-CH=CHMe.

While RH binding by (^{t}Bu$_3$SiN=)$_3$W (**2**) is considered strong, intramolecular exchange between alkane complex isomers must be rapid, assuming a direct correlation between **2**−RH vs **2**−R′H, etc. and the corresponding alkane-activated products **1**−R and **1**−R′, etc. As entries 4 and 5 show, [(^{t}Bu$_3$SiN=)$_3$WH]K (**2**−KH) and ethyl iodide generate (^{t}Bu$_3$SiN=)$_2$(^{t}Bu$_3$SiNH)WEt (**1**−Et),[28] but with CD_3CH_2I as the substrate, both **1**−CH_2CD_3 (14%) and **1**−ND−CD_2CH_3 (2%) are produced, with k_H/k_D = 7.9(5).[6,12,14,25] Presumably, C−H and C−D bound forms of **2**−CH_3CD_3 rapidly interconvert,[14] and the subsequent CH/D activation is devoid of pathways that scramble H and D among C_α and C_β. In support of **2**−RH/**2**−R′H equilibration, **2**−KH and benzyl iodide (entry 6) afforded only aryl-activated products, (^{t}Bu$_3$SiN=)$_2$(^{t}Bu$_3$SiNH)W(C_6H_4-*p*-CH_3) (**1**−C_6H_4-*p*-CH_3) and **1**−C_6H_4−*m*-CH_3[29] in a 1.4:1 ratio, while allyl iodide (entry 7) yielded (^{t}Bu$_3$SiN=)$_2$(^{t}Bu$_3$SiNH)W(*trans*-CH=CHMe) (**1**−*trans*-CH=CHMe).[30] These entries illustrate the propensity of early metal imido complexes to activate sp^2 over benzylic or allylic CH bonds.[15]

Further indications of selective CH bond activation, sp^2 over sp^3 [15] can be inferred from entries 8 and 9. Cyclopropylmethyl bromide reacted with **2**−KH to produce the *trans*-methylcyclopropyl derivative (^{t}Bu$_3$SiN=)$_2$(^{t}Bu$_3$SiNH)W(*trans*-(*c*-C_3H_4)Me) (**1**-*trans*-(*c*-C_3H_4)Me)[31] and a small amount of the ring-opened product (^{t}Bu$_3$SiN=)$_2$(^{t}Bu$_3$SiNH)W(*trans*-CH=$CHCH_2CH_3$) (**1**-*trans*-CH=$CHCH_2CH_3$), while 5-hexenyl bromide afforded **1**-*trans*-CH=$CH(CH_2)_3CH_3$.[32] While it is unknown whether the former reaction implicates radical character in RX reduction,[33] thermolysis of **1**−*trans*-(*c*-C_3H_4)Me for 2 d at 150 °C incurred no generation of **1**−*trans*-CH=$CHCH_2CH_3$. The migration of (^{t}Bu$_3$SiN=)$_3$W (**2**) from the carbon that has received the hydride to the ultimate activation site−5 carbons away in the case of (^{t}Bu$_3$SiN=)$_3$W(CH_2=$CH(CH_2)_3CH_3$) (**2**−1-hexene), and a traverse from methyl to the opposite side of the cyclopropane ring in **2**−(*c*-C_3H_5)Me−follows established selectivity trends.[15] The absence of C_6D_6 activation (<2%) in entries 6−9 indicates that the $\Delta G^\ddagger$ for RH loss from **2**−RH (RH = C_7H_8, C_3H_6, (*c*-C_3H_5)Me, and 1-hexene) is ≥2.3−2.9 kcal/mol.

Although the results are also consistent with a solvent cage comprised of (^{t}Bu$_3$SiN=)$_3$W (**2**) and RH, calculational studies strongly support the alkane adducts (^{t}Bu$_3$SiN=)$_3$W(RH) (**2**−RH) proposed (i.e., (HN=)$_3$W(CH_4); 23 °C, $\Delta H°_{bind}$ = −15.6 kcal/mol, $\Delta G°_{bind}$ = −8.4 kcal/mol).[19] Attempts to directly observe **2**−RH and efforts to understand the nature of hydride transfer between **2**−KH and RX, the energetics pertaining to selectivities, and the reactivity of additional substrates are underway.

Acknowledgment. We thank the National Science Foundation (Grant CHE-9528914) and Cornell University for support of this research, and Professor Thomas R. Cundari for helpful discussions.

JA980115R

(27) **2**−KI: ^{1}H NMR (C_6D_6, 23 °C) δ 1.53 (s, ^{t}Bu); ^{13}C{^{1}H} NMR δ 24.81 (SiC), 31.95 (CH_3).

(28) **1**−Et: ^{1}H NMR (C_6D_6, 23 °C) δ 1.20 (s, ^{t}Bu, 27 H), 1.34 (s, ^{t}Bu, 54 H), 2.06 (t, CH_3, 3 H, J = 7 Hz), 2.36 (q, CH_2, 2 H, J = 7 Hz), 6.51 (s, NH, 1 H); ^{13}C{^{1}H} NMR δ 19.67 (CH_3), 23.31 (HNSiC), 24.42 (=NSiC), 30.72 (HNSiCCH_3), 31.22 (=NSiCCH_3), 39.01 (CH_2, J_{WC} = 137 Hz).

(29) **1**−C_6H_4-*p*-CH_3: ^{1}H NMR (C_6D_6, 23 °C) δ 1.22 (s, ^{t}Bu, 27 H), 1.38 (s, ^{t}Bu, 54 H), 1.97 (s, CH_3, 3 H), 6.83 (s, NH, 1 H), 7.02 (d, ArH, J = 7 Hz), 8.39 (d, ArH, J = 7 Hz); ^{13}C{^{1}H} NMR δ 23.58 (HNSiC), 24.58 (=NSiC), 30.81 (HNSiCCH_3), 31.32 (=NSiCCH_3), 21.49 (CH_3). **1**−C_6H_4-*m*-CH_3: ^{1}H NMR (C_6D_6, 23 °C) δ 1.21 (s, ^{t}Bu, 27 H), 1.37 (s, ^{t}Bu, 54 H), 2.17 (s, CH_3, 3 H), 6.83 (s, NH, 1 H), 8.26 (m, ArH), 8.35 (s, ArH); ^{13}C{^{1}H} NMR δ 23.58 (HNSiC), 24.58 (=NSiC), 30.79 (HNSiCCH_3), 31.29 (=NSiCCH_3), 21.49 (CH_3). Remaining aryl resonances unassignable.

(30) **1**−*trans*-CH=CHMe: ^{1}H NMR (C_6D_6, 23 °C) δ 1.23 (s, ^{t}Bu, 27 H), 1.37 (s, ^{t}Bu, 54 H), 1.70 (dd, Me, 3 H J = 1.5, 6 Hz), 6.63 (s, NH, 1 H), 7.11 (C_βH, obscured), 8.01 (dq, C_αH, 1 H, J = 16, 1.5 Hz); ^{13}C{^{1}H} NMR δ 23.54 (HNSiC), 24.42 (Me), 24.53 (=NSiC), 30.78 (HNSiCCH_3), 31.26 (=NSiCCH_3), 153.46, 167.63 (C_α, C_β).

(31) **1**−*trans*-(*c*-C_3H_4)Me: ^{1}H NMR (C_6D_6, 23 °C) δ 1.06 (m, *t*-CH*H*, 1 H), 1.14 (d, Me, 3 H, J = 6 Hz), 1.24 (s, ^{t}Bu, 27 H), 1.35 (s, ^{t}Bu, 54 H), 1.65 (m, WCH, 1 H), 1.89 (m, *c*-CH*H*, 1 H), 2.09 (m, CHMe, 1 H), 6.03 (s, NH, 1 H); ^{13}C{^{1}H} NMR δ 21.92 (CH_3), 22.66, 22.97 (C_β, C_β′), 23.44 (HNSiC), 24.40 (=NSiC), 30.79 (HNSiCCH_3), 31.22 (=NSiCCH_3), 49.48 (C_α, J_{WC} = 187 Hz).

(32) **1**−*trans*-CH=$CH(CH_2)_3CH_3$ δ 0.84 (t, CH_3, 3 H, J = 7 Hz), 1.24 (s, ^{t}Bu, 27 H), 1.36 (s, ^{t}Bu, 54 H), 2.06 (m, CH_2, 2 H), 6.62 (s, NH, 1 H), 8.01 (d, C_αH, 1 H, J = 17 Hz); ^{13}C{^{1}H} NMR δ 23.57 (HNSiC), 24.54 (=NSiC), 30.80 (HNSiCCH_3), 31.26 (=NSiC-CH_3), 22.37, 24.95, 31.89, 38.50 ((CH_2)$_3$-CH_3), 158.90, 166.19 (C_α, C_β).

(33) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317−323.